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Effect on Properties of Reduced Size and Dimensions

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I. INTRODUCTION

In the last decade, materials science has witnessed substantial progress in the synthesis, characterization, and understanding of materials with atomic dimensions [1,2]. Using a variety of techniques such as ball milling, sputtering, chemical vapor deposition, lithography, sol gel formation, scanning tunneling microscopy, and supersonic molecular beams, it is possible to generate materials with dimensions and sizes ranging from a few angstroms to several nanometers. These include, for example, multilayers, chains of atoms and atomic clusters on surfaces, quantum dots, three-dimensional nanostructure films, nanoscale materials, and small atomic clusters. The electronic, magnetic, optical, and chemical properties of these materials have been found to be very different from those of the bulk form and to depend sensitively on size, shape, and composition. For example, small clusters of transition metal atoms have been found to have reactivities that are considerably larger than those of the bulk metal and vary by orders of magnitude with size [3]. Clusters of nonmagnetic solids have been found to exhibit magnetic

order [4]. Nanocomposites are showing giant magnetoresistance [5,6], enhanced remanence [7], and other magnetic materials features. These developments are adding new frontiers to materials science and are raising hopes of generating new materials [8] with any desirable combination of properties by assembling, for example, suitably chosen clusters or nanoparticles.

In this chapter we review how material properties change as one starts with single atoms and brings them together to form a bulk or vice versa. The most dramatic changes occur at small sizes, and since developments in experimental techniques are giving hope that it may soon be possible to assemble materials composed of very small particles, we include small clusters in our discussion. It is difficult to review all the areas in a single chapter, but I will take selected examples to illustrate how the geometrical arrangements and thermal, electronic, and magnetic properties change as size or dimension changes. As I will show, the magnetic properties are the ones that are most affected by the change in size and present several new features. They are also the ones with potential for numerous applications. I therefore place extra emphasis on novel phenomena in the area of magnetism.

II. EVOLUTION OF GEOMETRY AND PHYSICAL PROPERTIES

One of the basic questions has been that of how the geometrical arrangement of atoms and their stability change with size. Starting from the bulk, the first effect of reducing particle size is to create more surface sites. This changes the surface pressure and results in a change in the interparticle spacing. This effect is shown in Fig. 1 for the case of small Cu_n particles [9]. It is interesting to note that the interparticle spacing decreases with size. This can be understood as due to competition between the long-range electronic forces and the short-range core–core repulsion. This decrease in interparticle spacing with decreasing size is typical of metal clusters. For semiconductors or many metal oxides, there are indications that the interparticle spacings increase with decreasing size. Although the main effect at large particle sizes is the change in interparticle spacing, more drastic changes occur if the size is further reduced. The atoms can arrange themselves in
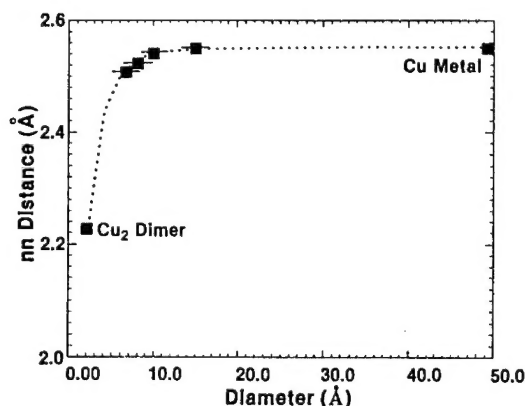
Figure 1 Interatomic distance in Cu_n as a function of size. (From Ref. 9.)

geometrical patterns forbidden in the bulk solids. For example, large clusters of Ca_n [10] and several other metals generated in molecular beams have been found to be icosahedral. The change in geometry continues to very small sizes containing only a few atoms, at which point all traces of the bulk arrangement may be lost [11]. It is clear that at these sizes the clusters are no longer fragments of the bulk structure.

The change in interparticle spacing and the larger surface-to-volume ratio in particles has a concomitant effect on material properties. Variations in the surface free energy change the chemical potential. This affects, for example, the thermodynamic properties, of which the simplest example is the melting point. Figure 2 shows the melting point of Au_n particles as a function of size [12,13]. Note that the melting point decreases with size and the rate of decrease increases substantially at very small sizes. There are indications that the monotonic decrease changes to nonmonotonic fluctuations at very small sizes [14].

III. EVOLUTION OF THE ELECTRONIC SPECTRUM AND CHEMICAL PROPERTIES

The variations in interparticle spacing and geometry also result in a variation in electronic properties with size. As the size is reduced from the bulk, the electronic bands in metals become narrower and the
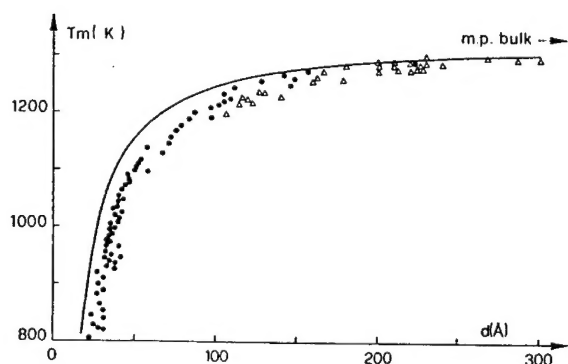
Figure 2 Melting point of small Au_n particles as a function of size. (From Ref. 12.)

delocalized electronic states are transformed to more localized molecular bonds. It is interesting to ask, At what size does a particle of metallic atoms behave like a bulk metal? Does this transition occur gradually or spontaneously? It has been difficult to answer these questions theoretically or experimentally. The electronic quantity most easily accessible to experiments is the ionization potential. Over the past few years, there have been numerous studies of the ionization potentials of clusters of various elements as a function of size [15]. They show that the ionization potentials at small sizes are higher than the bulk work function and show marked fluctuations as a function of size. For example, for K_n clusters, measurements [16] show dips in the measured potential for clusters containing 8, 18, 20, 40, 58, 92, . . . atoms. These dips have been explained within a simple model, where the cluster is described as a Jellium sphere [16], as arising due to filling of the electronic levels. They also correspond to enhanced stability at these sizes.

A technique currently being used to probe the changes in electronic spectrum with size is the photoelectron spectroscopy of free clusters. Here, one generates negatively charged clusters in molecular beams by exposing clusters to low energy electrons. The anionic clusters are then crossed with a fixed frequency laser beam and the resulting photodetached electrons are analyzed. The spectra are fingerprints of the ground and excited states of the neutral cluster. They therefore provide

information on vertical and adiabatic electron affinities and the low-lying electronic states. In particular, the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is a signature of the transition to the metallic regime. This technique has been used for a variety of clusters ranging from C [17], through the semiconducting elements Si and Ge [18], to the metallic elements Na, K, Al, Fe, Co, and Cu [19]. To provide an example, Fig. 3 shows the variation of the vertical electron affinities (E.A.) and HOMO–LUMO gap (ΔE_{HL}) in Cu_n clusters measured by Pattiette et al. [20]. Note that the clusters containing 8, 20, and 40 atoms have low electron affinities and larger HOMO–LUMO gaps, and, as mentioned above, these can be related to the filling of the electronic shells.

The large surface-to-volume ratio and the variations in geometry and electronic structure have a strong effect on catalytic properties. As an example, the reactivity of small clusters has been found to vary by
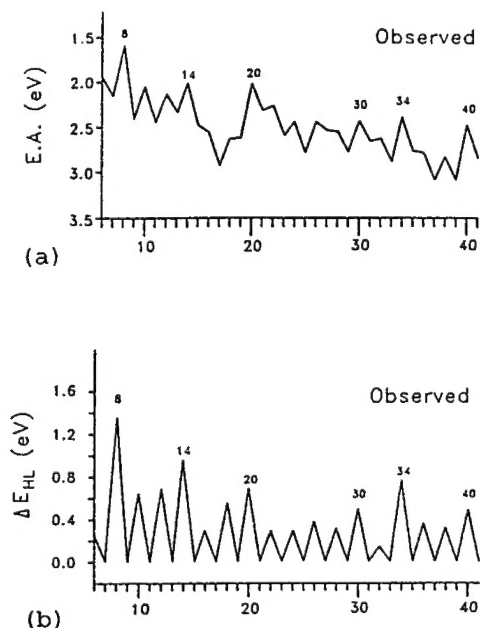

(a)

(b)

Figure 3   (a) Measured vertical electron affinities and (b) HOMO–LUMO gaps in Cu_n clusters. (From Ref. 20.)

orders of magnitude when the cluster size is changed by only a few atoms [3]. Figure 4 shows this for the case of Fe_n clusters reacting with hydrogen. Another example with potential for applications is hydrogen storage in metals. It is well known that most metals do not absorb hydrogen, and even among those that do, hydrogen is typically adsorbed dissociatively on surfaces with a hydrogen-to-metal ratio of 1. This limit can be significantly enhanced in small sizes. Cox et al. [21] showed that small positively charged clusters of Ni, Pd, and Pt generated in molecular beams and containing between two and 60 atoms can absorb up to eight hydrogen atoms per metal atom. The number of absorbed atoms decreases with increasing cluster size and approaches one for clusters having around 60 atoms. This shows that small particles may be very useful in hydrogen storage devices. Yet another case of the effect of size on properties is provided by nanophase powders of lithium magnesium oxide, which have been found to show threshold catalytic activity at temperatures much below the bulk limits [22].
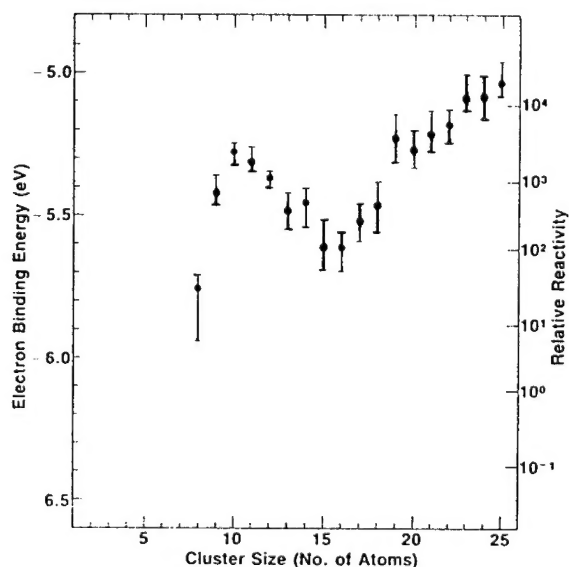

Figure 4 Ionization potential and reactivity of Fe_n clusters as a function of size. (From Ref. 3.)

IV. MAGNETISM IN PARTICLES OF REDUCED SIZE AND DIMENSIONS

The most tantalizing effects of size are observed in the case of magnetic properties. A bulk ferromagnet is characterized by domains that each contain several thousand atomic spins. The spins are aligned within the domain, but different domains point in different directions. The ferromagnetic phase transitions correspond to the establishment of a long-range magnetic order where the domains become aligned. One would have thought that by going to smaller sizes, i.e., clusters or nanoparticles, the absence of domain walls and long-range correlations would result in a simpler system. The reality is quite the opposite. Small particles of magnetic and even nonmagnetic solids exhibit a totally new class of magnetic properties marked by quantum effects that are far from being completely understood [23–25]. Table 1 gives a brief summary of the observed magnetic behavior of very small particles of various metals vis-à-vis their behavior in bulk. Note the qualitative change in behavior in almost all cases. These differences show that nanomaterials could have important applications in magnetic areas such as nonvolatile magnetic storage, sensing devices, and hard permanent magnets.

The magnetic properties of particles combine the effects of the reduced dimensions of the surface sites and the reduced volume. The effect of dimension is particularly interesting, because many new effects have been observed in bulk multilayers. For example, multilayers of magnetic and nonmagnetic elements have been found to exhibit oscillatory exchange coupling [26]. Ferromagnetic and antiferromagnetic multilayers have been found to exhibit giant magneto-

Table 1   Behavior of Metals in Bulk and in Smaller Sizes

Metal	Bulk	Cluster
Na, K	Paramagnetic	Ferromagnetic
Fe, Co, Ni	Ferromagnetic	Superparamagnetic
Gd, Tb	Ferromagnetic	Rotors/superparamagnetic
Cr	Antiferromagnetic	Frustrated paramagnetic
Rh	Paramagnetic	Ferromagnetic

resistance (GMR) [27], which arises because of the differences in spin-dependent electron scattering from the ferromagnetic and antiferromagnetic layers. These effects are carried over to the domain of nanostructured materials with additional contributions from the finite size.

A. Variation of the Magnetic Moment with Size

Small particles differ from the bulk solids in that a large fraction of the atoms reside at the surface. These atoms have lower coordination numbers than the interior atoms. Further, depending on the geometry, different sites on the surface will differ in local coordination number. Some general considerations of the variation of moment with local environment can thus give an idea of the magnetic moment of large clusters vis-à-vis the bulk. This prompted Liu et al. [27] to conduct a series of theoretical investigations of the dependence of the magnetic moment of Fe, Co, and Ni sites in various situations such as bulk, slabs, planes, and chains. The results showed that the local moment was primarily determined by the local coordination number. Figure 5 shows
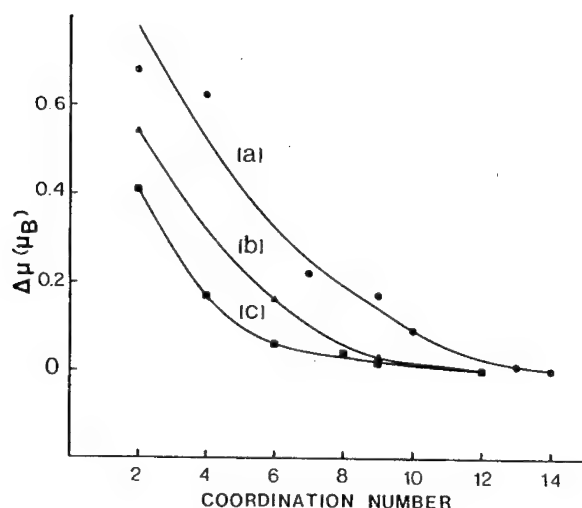

Figure 5 Deviation from the bulk magnetic moment in (a) Fe, (b) Co, and (c) Ni as a function of nearest neighbor coordination (in various structures).
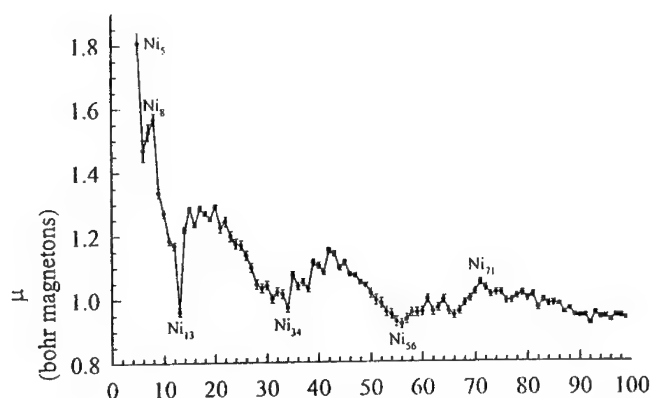
Figure 6 Magnetic moments in Ni_n particles as a function of size. (From Ref. 29.)

the calculated dependence of the magnetic moment on the nearest coordination number. It is clear that as the coordination number decreases, the moment increases toward the atomic value.

These studies suggested that small particles should be more magnetic than the bulk material. This is indeed found to be the case. The recent experiments by Chen et al. [28] on Co_n particles in the range of 1.8–4.4 nm showed that the magnetic moment of particles of ~1.8 nm was about 20% higher than that of the bulk. The enhancement in moment continues gradually as the size is reduced, but at very small sizes the monotonic increase is replaced by a discontinuous dependence of moment on the particle size. Figure 6 shows the recently measured moments of Ni_n clusters [29]. Note that a Ni_5 cluster has almost three times the moment per atom compared to bulk Ni. Further, the moment shows dips at $n = 13, 55, \ldots$. These variations are associated with the detailed changes in the electronic states and the atomic packing.

V. MAGNETISM IN CLUSTERS OF NONMAGNETIC SOLIDS

Most atoms and molecules have nonzero spin multiplicities, but only a few solids are magnetic. How does the transition from atomic to bulk magnetic properties take place? Can clusters of nonmagnetic solids be
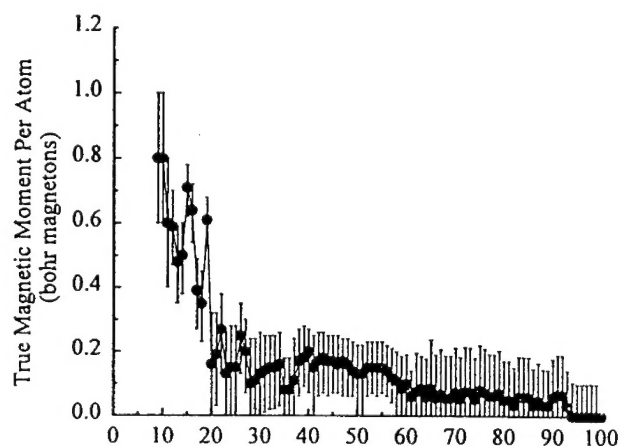
Figure 7 Magnetic moments in Rh$_n$ particles as a function of size. (From Ref. 31.)

magnetic? This issue was addressed by Reddy et al. [30], who undertook a study of the 13-atom icosahedral clusters of the 4*d* elements Rh, Pd, and Ru. They found that the central and outer atoms in the icosahedral cluster had magnetic moments of 1.58 μ_B and 1.62 μ_B, respectively. Following the theoretical prediction, Cox et al. [4] experimented with small Rh$_n$ clusters containing 12–32 atoms in Stern–Gerlach arrangement. They found that the clusters are indeed magnetic, in agreement with the prediction! Later experiments [31] on 9–100-atom clusters showed that the moment changes dramatically with size and that clusters containing 9, 10, 11, 15, ... atoms are more magnetic than their neighbors. Figure 7 shows their experimental results. Note that the magnetism is special to small sizes and disappears in clusters containing more than 80 or so atoms. This is the first case where a solid has been shown to spontaneously become magnetic at small sizes. In addition to free clusters, clusters of nonmagnetic elements supported on metal substrates have also bee proposed to be magnetic [32].

VI. MAGNETIC BEHAVIOR OF SMALL PARTICLES

In the foregoing text, we mainly focused on the variation of magnetic moment with size. The reduction in size also leads to a modification of

the magnetic behavior. The particle sizes are usually smaller than domain sizes in solids, and the atomic spins are exchange-coupled. The particle therefore behaves like a single atom with a large moment. The reduction in size leads to a decrease in the anisotropy energy. The moment can therefore fluctuate from one to another direction via thermal energy or quantum tunneling. Above a certain temperature called the blocking temperature, there is enough thermal energy for the particle to behave like a paramagnetic atom with a large moment. This behavior is called superparamagnetism and is observed in small particles [33] as well as very small clusters [34]. The dependence of the blocking temperature on size is interesting and has been measured by Chen et al. [28] for the case of nanophase Co_n particles. It decreases from 50 to 19 K as the size of the particles is decreased from 4.4 to 1.8 nm. The coercivity of the particles at 10 K decreased from 1250 to 640 Oe as the particle size decreased from 4.4 to 1.8 nm. The anisotropy constants re also found to increase as the size is reduced. In nanophase Fe particles, the anisotropy constants are an order of magnitude higher than in bulk Fe.

New exciting developments are coming from synthesis of materials consisting of coupled nanostructures. For example, ball milled Nd-Fe-B magnets [7] have been found to have enhanced remanence with smaller grain sizes. This has applications in the development of hard magnets. Another interesting development is the discovery of GMR in granular alloys composed of magnetic grains or clusters less than 10 nm in size [35,36]. Finally, three-dimensional nanostructures of nanoclusters encapsulated in cages or deposited on surfaces in geometrical patterns are showing a completely new phenomenon. Hehn et al. [37] recently made an array of 25 nm thick cobalt dots on Al_2O_3 substrate. By varying the thickness of the dots, these authors observed a series of spin configurations including vortices.

VII. CONCLUSION

This review has shown that the physical, electronic, magnetic, and chemical properties of materials depend sensitively on size and that small particles display behaviors that are different from those of the individual atoms or bulk. The new behaviors are not only important from a fundamental point of view but also lead to new applications. In fact, the ability to control properties by changing size, composition, or

dimension shows that nanoscale materials will form the basis of a new class of atomically engineered materials with tailored properties.

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